Composite Film via Solvent Casting Method of Carboxymethyl Cellulose/Citric Acid/Artificial Humus and Their Potential in Controlled Release of Urea Fertilizer

Ramlah, Sutarno, and Indriana Kartini*

Departement of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta, Indonesia
Email: ramlah1998@mail.ugm.ac.id (R.); sutarno@ugm.ac.id (S.); indriana@ugm.ac.id (I.K.)
*Corresponding author

Manuscript received Month date, 2024; revised June 4, 2024; accepted June 11, 2024; published September 20, 2024

***Abstract*—Macronutrient fertilizers, especially Nitrogen (N), have contributed greatly to increasing agricultural production. However, high fertilizer concentrations and uncontrolled leaching of nutrients lead to an increase in unwanted unassimilated reactive nitrogen and cause environmental pollution. This study aims at producing film with slow-release fertilizer. The bioplastic composite was prepared by solvent casting method employing Carboxymethyl Cellulose (CMC) as the plastic matrix, citric acid as a crosslinker, urea as nitrogen source and artificial humus as slow-release agent. Mechanical and water absorption tests were conducted to determine the physical properties of the film, while X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) analysis to evaluate their chemical properties. The release of urea was accessed through UV Vis spectroscopy. The optimum condition of composite bioplastics was obtained at the composition of 4.5% CMC, 3% citric acid, and 10% (w/v) of artificial humus with a tensile strength of 11.59 MPa and elongation at break of 28.67%. release behavior shows the release of pure urea particles in water was almost 100% while release rate of urea from the composite in water is only about 11.5% in 48 h.**

***Keywords*—carboxymethyl cellulose, citric acid, artificial humus, urea, slow-release fertilizer**

I. Introduction

Urea is one type of fertilizer that is widely used in agriculture because of its high nitrogen content, which reaches 46% and its affordable price [1]. Nitrogen is the most important element and is the main element for plant health, growth, development and good production [2]. Nitrogen is often required in the most abundant amounts compared to all other mineral elements as it plays an important role in most plant physiological processes [3]. However, the nitrogen use efficiency of urea fertilizer is still relatively low, which is only around 30–35% [4].

Meanwhile, about 30%–50% of fertilizer nutrients are lost through various means, resulting in a series of environmental problems such as water eutrophication, groundwater pollution, air pollution and soil quality degradation [5]. This is because urea fertilizer has low thermal stability and high solubility so that the nitrogen content is easily mobilized [6]. The mobilization process occurs through volatilization in the form of NH_3 gas, dissolved by surface water (run-off) and leaching into the soil in the form of NO^{3-} ions and emits N_2O and N_2 gas as a result of denitrification which results in a decrease in nutrient availability for plants [7]. This is a major challenge for farmers around the world, as N loss leads to wasted economic costs and environmental pollution.

Slow-release fertilizers are specially designed to improve the effective use of chemical fertilizers by controlling the rate of nutrient release gradually according to the needs of plants [8]. This not only improves fertilizer efficiency, but also reduces the frequency of fertilization and the total amount of fertilizer used and reduces environmental problems caused by excessive use of chemical fertilizers. In addition, the release rate of slow-release fertilizers has been shown to be more in line with that required for plant physiological functions [9].

Artificial humus is a substrate rich in humic acid content with functional groups such as carboxyl (–COOH), hydroxyl (–OH), and carbonyl (–C=O) groups and contains ion exchange groups that are able to complex or absorb nutrients [10]. The high porosity of artificial humus further increases its capacity to absorb and adsorb nutrient ions on its porous surface [11].

In recent years, film-based slow-release fertilizers have begun to be developed. It is also expected to replace the use of the film materials that are made of petroleum-based materials such as polyethyleneimine, polyacrylic acid and polyolefins, organic polymers are usually toxic and non-biodegradable [12], which may cause a series of environmental problems such as accumulation of soil toxicity, consumption of fossil energy and irreversible damage to soil [1].

Carboxymethyl Cellulose (CMC) is one of the cellulose-derived polymers that is widely used as a film matrix because it is easily degradable, non-toxic, relatively cheap and able to provide flexible properties to the film [8]. However, one of the disadvantages of carboxymethyl cellulose when applied as a film is that it is easily soluble in water, so a crosslinking agent is needed to reduce the solubility of carboxymethyl cellulose in water media. Citric acid is a widely used environmentally friendly crosslinker that provides improved water stability to polymer matrices to form hydrogels and composites [13]. The use of citric acid as a crosslinker is not only limited to its non-toxicity, but also because citric acid forms stable crosslinks with polymers containing high-density hydroxyl groups [14].

II. Literature Review

A. Slow-Release Urea Fertilizer

Urea fertilizer with the molecular formula $CO(NH_2)_2$ is a widely used type of fertilizer due to its high nitrogen content (46%) and affordable price [15]. Nitrogen is an essential nutrient required by plants. Nitrogen not only plays an important role in the formation of plant proteins and nucleic acids on which growth is based, but also provides essential elements for producing chlorophyll (the organ of photosynthesis), enzymes, vitamins, alkaloids, plant hormones, and other materials that are closely related to crop yield and quality [16]. Once applied to the soil, urea fertilizer undergoes a number of biological, chemical and physical changes to supply plant-available nutrients. These changes include the formation of NH^{4+} cations and NO^{3-} anions that will be absorbed by plant roots [17].

However, if the presence or concentration of urea dissolved in water and soil is too much, it will be broken down into N_2, N_2O and NH_3 gas. These processes can cause negative impacts such as water eutrophication, groundwater pollution, air pollution, and soil quality degradation [5]. Therefore, a method is needed to regulate the release rate of urea fertilizer so as to control the loss of nitrogen nutrients, increase the efficiency of nitrogen uptake by plants and reduce the risk of pollution in agricultural ecosystems due to fertilizer use. Slow-Release Fertilizer (SRF) or commonly known as slow-release fertilizer is one method that can be used to regulate the release rate of urea. SRF can be defined as a fertilizer that extends the availability of nutrients for plant uptake after application. When compared to conventional fertilizers, SRF has a lower nutrient release rate, is able to extend the availability of nutrients for plant uptake and reduce nutrient losses to the environment [18].

B. Artificial Humus as Slow-Release Agent

Humus substances play a vital role in plant nutrition and soil fertility. Plants grown on soils which contain humus are less stressed, healthier and more productive and harvested food foods have a better quality [19]. Humus can be divided into humic acid and fulvic acid according to their molecular characteristics and functions [20]. Fulvic acid may directly eliminate pathogens by inhibiting their mycelial growth [20]. Humic acid benefits plant growth by promoting cell growth, photosynthesis, endogenous hormone biosynthesis, phosphate uptake and secondary metabolites production [21].

Humic acid is a polyelectrolyte macromolecular compound rich in functional groups (i.e. carboxyl, phenolic hydroxyl and quinone groups), providing the possibility to incorporate exogenous N into its structure through chemical reactions [22]. However, most humic acid applicated in for agricultural production and environmental protection currently refers to the species formed in soil, peatlands or lake [23], which obviously limited the large-scale applications of humic acid, considering the non-renewable of natural resources. Furthermore, the unpredictable diversity and structural heterogeneity are another limiting factor for humic acid being extensively used [24]. Thus, developing new methods of producing humic acid from renewable sources is urgently needed for sustainable development.

However, the production of humus is slow due to the rate of biological metabolism and is limited by microbial contamination and foul odors [25]. Hydrothermal processing is a quick and efficient method to convert biomass of wet wastes to more valuable materials, while avoiding energy consumption during the drying process which was later named artificial humus [26].

C. Film Based Slow-Release Fertilizer

In recent years, film-based slow-release fertilizers have begun to be developed. Carboxymethyl cellulose has non-toxic, odorless, water-soluble, and thermally stable characteristics, making it capable of forming flexible and strong films [27, 28]. Some studies show that carboxymethyl cellulose-based films are superior when compared to other polysaccharides due to their high molecular weight and molecular interactions [29]. This makes carboxymethyl cellulose a promising biopolymer to replace non-degradable polymers in various applications [30].

However, the utilization of carboxymethyl cellulose as a bioplastic matrix still has limitations in the form of weak water resistance [29]. This is not only limited to carboxymethyl cellulose but almost all biodegradable films have low water resistance [31]. The limitations of carboxymethyl cellulose can be overcome by modifying it through blending with other polymers [32] or modifying it by adding cross-linking agents such as citric acid [33]. Salihu [13] also confirmed that carboxymethyl cellulose-based films use citric acid as a cross-linking agent.

Citric acid is a small molecule organic acid with biodegradable and non-toxic properties. Citric acid is easily dehydrated and forms a reactive anhydrous that can undergo esterification crosslinking reactions with hydroxyl (–OH) groups on other polymers [34, 35]. Habibi [36] revealed that the interaction between KMS and citric acid occurs through the hydroxyl group (–OH) at the end of the KMS chain (KMS backbone) will bind to the carboxyl group of citric acid to form a KMS-KMS interpolymer interaction.

III. MATERIALS AND METHODS

A. Materials

Carboxymethyl cellulose, Urea (CH_4N_2O), citric acid ($C_6H_8O_7$), artificial humus, 4-dimetilamino benzaldehida (4-$(CH_3)_2NC_6H_4CHO$), ethanol (C_2H_6O), Hydrochloric acid (HCl), aquades (H_2O) procured from Sigma Aldrich.

1) Preparation of artificial humus suspension contains urea (AH@Urea)

0.15 g of urea (the urea content was calculated by sowing about 10 g/m^2) were dissolved in 5 mL H_2O and 5 mL of various artificial humus (0%, 5%, 10%, 15%, and 20% w/v) were sonicated for 15 mins.

B. Preparation of Carboxymethyl Cellulose/citric Acid Film

Using the casting method, a CMC/CA was produced. Initially, 60 mL CMC 4.5% and 50 mL CA 3% were mixture and stirred for 1 hour. The homogeneous mixture was then poured into a 10 × 13 cm glass meld and dried in a 60 ºC blast oven for 24 h. The resulting film were tested for mechanical properties and water solubility.

C. Release Behavior of the AH@Urea-loaded CMC/CA Film in Water

0.1 g of the film immersed in 10 mL of H_2O, and after 0, 1, 3, 7, 24, 48 h of release, 4 mL of each film solution was collected. The phenol colorimetric method was used for the color reaction. The amount of urea released from the water was determined using a UV spectrophotometer.

D. Characterization

The film was characterized by X-Ray Diffraction and Fourier Transformation Infrared Spectroscopy (ATR-FTIR) in a range from 4,000 to 600 cm^{-1}.

IV. Result and Discussion

A. Mechanical Property

The effect of AH addition on the mechanical properties of films is shown in Fig. 1. It could be seen that the tensile strength of the film increased first and then decreased with the increase of artificial humus but the addition of artificial humus decreased elongation properties of the films. Humus substances contain humic acids that rich in functional groups i.e. carboxyl that reacted with urea to form humic acid/urea complexes. Further, the complexes crosslinked with CMC/AS to form a relatively dense network structure, which improved the tensile strength of the film [23]. Too much humic acid will lead to the excessive crosslinking density of the system and the gradual decrease of the mechanical properties. The best mechanical properties of the film were obtained when 10% AH was added, and the tensile strength and elongation of the film could reach 13.89 MPa and 29.92%, respectively.

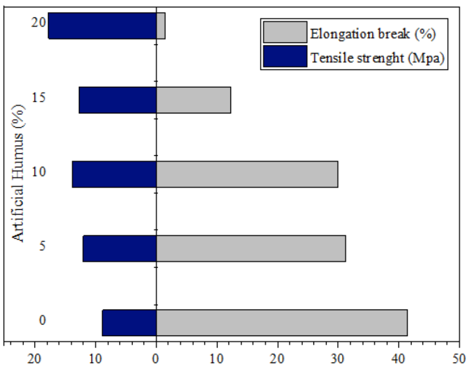

Fig. 1. Effect of different AH addition on the mechanical properties of the film.

B. Water Contact Angle and Water Absorption

To investigate the effect of AH addition on the hydrophobicity of the films, we examined the contact angle. As shown in Fig. 2(a) the contact angle of the film decreased with the increase of AH content. It is because of a large number of hydroxyl groups in AH, which are more hydrophilic than film without AH. Fig. 2(b) shown that the addition of AH increases water absorption. Due to its hydrophilic nature, AH can absorb water molecules and increase the water content of the film. In addition, humic acid/ urea complexes introduced many hydrogen bonds that had certain hydrophilicity [23].

C. FTIR and XRD Analysis

FTIR spectra provide information about the interactions between the functional groups of the different components. The FTIR spectra of components of the film are shown in Fig. 3 (a). The spectrum of pristine CMC shows a small peak at 2,924 cm^{-1} related to the asymmetric C-H stretching, and a band at 3,425 cm^{-1} attributed to the O-H stretching. The peaks at 1,419 and 1,589 cm^{-1} are ascribed to symmetric and asymmetric stretching vibrations of the carboxylate groups, respectively [37]. Additionally, the C-O-C stretching vibration of the polysaccharide skeleton can be observed at 1,057 cm^{-1} [8], and the O-H bending vibration is found at about 1327 cm^{-1} [38].

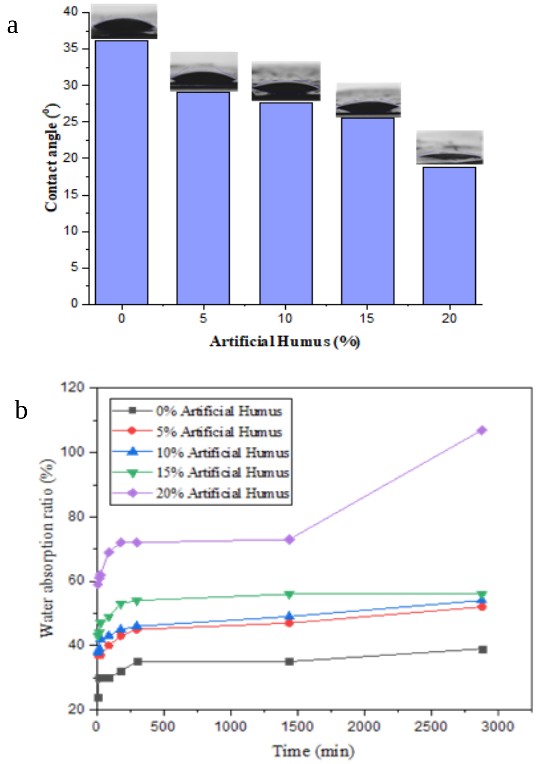

Fig. 2. Effects of different AH additions on the film: (a) contact angle and (b) water absorption.

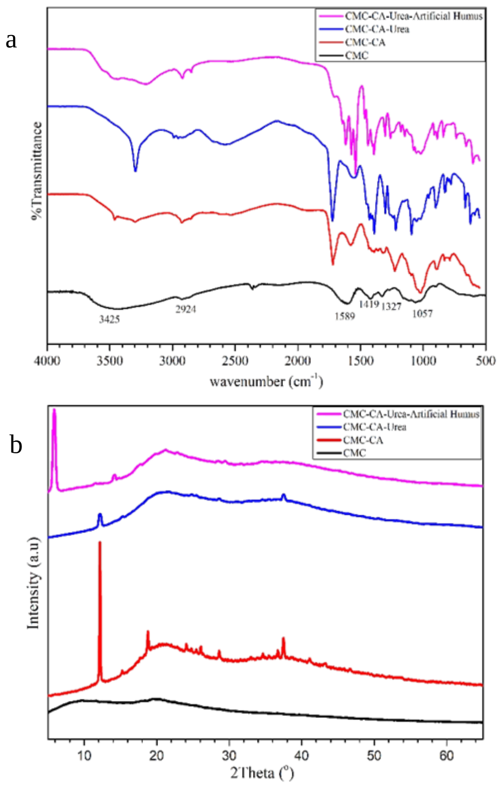

Fig. 3. (a) FTIR spectra of film; (b) XRD patterns of film.

The spectrum of the CMC/CA mixture shows that CA acts as a crosslinker through the formation of ester groups between the carboxyl groups of CMC and the hydroxyl groups of CA. This is reinforced by the appearance of a strong absorption band at 1,719 cm^{-1} along with a shift and decrease in the intensity of the absorption band at 3,461 cm^{-1}. After addition artificial humus in composite, the double bond characteristic peak of urea did not appear in 3,500–3,300 cm^{-1}, indicating that it might be covered by hydrogen bond or existed as a complex form of urea and humic acid. The stretching vibration peak of the C=O double bond of humic acid/urea complexes at 1,644 cm^{-1} confirmed that reaction did occur between urea and humic acid.

X-ray powder diffraction is a useful technique to get information about the crystal structure. The XRD patterns of CMC, CMC/CA, CMC/CA/Urea and CMC/CA/Urea/AH composite are shown in Fig. 3(b). The broad peak centered at $2\theta = 20.54°$ in the pattern of CMC is indicative of its amorphous structure [39]. The addition of citric acid causes an increase in intensity as well as a peak shift to $2\theta = 24.5°$. While the addition of urea or artificial humus does not provide significant changes, over all it can be said that this composite film is amorphous.

D. Release Behavior

The release rates of the urea in composite and pure urea are listed in Fig. 4. The release of pure urea particles in water was almost 100% in 48h without stirring. If compared to the release rate of urea from the composite in water, it shows a gradual release and within 48 h the release rate is only about 11.5%. Based on the nutrient release of no more than 15% within 24h, the composite can be categorized as a category 1 slow-release fertilizer when referring to the international standard ISO18644, which defines three specific criteria. First, within the first 24 hours after application, the fertilizer must not release >15% of its nutrients. Second, in the first 28 days after application, the release must not exceed 75%. Third, by the specified release date, about 75% of the total nutrient content should be released [40].

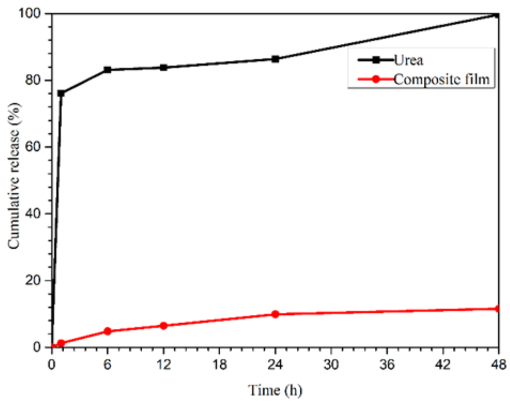

Fig. 4. Release behaviors of urea in water.

V. Conclusion

The current fertilization system adversely affects the environment and wastes fertilizer use. In this study, CMC/CA/AH/Urea slow-release fertilizer was synthesized using the solvent casting method to improve the effectiveness of fertilizer use. The addition of artificial humus at 10% gave the best mechanical properties of the film. incorporating urea into the composite film showed controlled release when compared to the application of urea directly in the environment.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Ramlah: Conducted the research, validation, formal analysis, investigation, and writing the original draft.

Indriana Kartini: Conceptualization, validation, formal analysis, writing-review, and editing.

Sutarno: Validation, formal analysis, writing-review and editing.

Funding

This research was funded by the Indonesia Endowment Fund for Education (LPDP) under the Ministry of Finance, Indonesia.

Acknowledgment

This research was funded by the Indonesia Endowment Fund for Education (LPDP) under the Ministry of Finance, Indonesia and Universitas Gadjah Mada for funding this conference.

References

[1] H. Zhang, X. Wei, and L. bin *et al.*, "Preparation and characterization of biochar-based slow-release nitrogen fertilizer and its effect on maize growth," *Ind. Crops Prod.*, vol. 203, no. 6, 117227, 2023.

[2] J. Martínez-Dalmau, J. Berbel, and R. Ordóñez-Fernández, "Nitrogen fertilization. A review of the risks associated with the inefficiency of its use and policy responses," *Sustain.*, vol. 13, no. 10, pp. 1–15, 2021.

[3] A. Iqbal, Q. Dong, and X. Wang, "Nitrogen preference and genetic variation of cotton genotypes for nitrogen use efficiency," *J. Sci. Food Agric.*, vol. 100, no. 6, pp. 2761–2773, 2020,

[4] M. Ullah, M. Zahid, S. M. All-e-raza, Q. Ghulam, M. Qureshi, and F. Ali, "Do green supply chain management practices improve organizational resilience during the COVID-19 crisis? A survival analysis of global firms," *Econ. Lett.*, vol. 2, no. 8, 110802, 2022.

[5] S. Marchuk, S. Tait, P. Sinha, P. Harris, D. L. Antille, and B. K. McCabe, "Biosolids-derived fertilisers: A review of challenges and opportunities," *Sci. Total Environ.*, vol. 875, 162555, 2023,

[6] T. Zhou, Y. Wang, S. Huang, and Y. Zhao, "Synthesis composite hydrogels from inorganic-organic hybrids based on leftover rice for environment-friendly controlled-release urea fertilizers," *Sci. Total Environ.*, vol. 615, pp. 422–430, 2018.

[7] S. K. Das and G. K. Ghosh, "Developing biochar-based slow-release N-P-K fertilizer for controlled nutrient release and its impact on soil health and yield," *Biomass Convers. Biorefinery*, 2021.

[8] C. Banik, S. Bakshi, D. A. Laird, R. G. Smith, and R. C. Brown, "Impact of biochar-based slow-release N-fertilizers on maize growth and nitrogen recovery efficiency," *J. Environ. Qual.*, vol. 52, no. 3, pp. 630–640, 2023.

[9] Z. Yang, W. Su, J. Fang, Y. Qian, and H. Li, "A degradable mulch film with fertilizer slow-release function enhanced by lignin," *ACS Applied Polymer Materials*, vol. 5, no. 9, pp. 6864–6874, 2023.

[10] F. Yang, C. Tang, and M. Antonietti, "Natural and artificial humic substances to manage minerals, ions, water, and soil microorganisms," *Chem. Soc. Rev.*, vol. 50, no. 10, pp. 6221–6239, 2021

[11] Y. Jin, X. Zhang, Y. Yuan, Y. Lan, K. Cheng, and F. Yang, "Synthesis of artificial humic acid-urea complex improves nitrogen utilization," *J. Environ. Manage.*, vol. 344, no. 3, 118377, 2023.

[12] S. Zhang, S. Zhang, and S. Zhang *et al.*, "Self-assembly of hydrophobic and self-healing bionanocomposite-coated controlled-release fertilizers," *ACS Appl. Mater. Interfaces*, vol. 12, no. 24, pp. 27598–27606, 2020.

[13] R. Salihu, S. I. Abd Razak, and N. A. Zawawi *et al.*, "Citric acid: A green cross-linker of biomaterials for biomedical applications," *Eur. Polym. J.*, vol. 146, no. 11, 110271, 2021.

[14] M. M. Hassan, N. Tucker, and M. J. L. Guen, "Thermal, mechanical and viscoelastic properties of citric acid-crosslinked starch/cellulose composite foams," *Carbohydr. Polym.*, vol. 230, 115675, 2020.

[15] N. Kottegoda, C. Sandaruwan, and G. Priyadarshana *et al.*, "Urea-hydroxyapatite nanohybrids for slow release of nitrogen," *ACS Nano*, vol. 11, no. 2, pp. 1214–1221, 2017.

[16] Y. Li, Y. Lv, M. Lian, F. Peng, and Y. Xiao, "Scientia horticulturae effects of combined glycine and urea fertilizer application on the photosynthesis , sucrose metabolism , and fruit development of peach," *Sci. Hortic. (Amsterdam).*, vol. 289, no. 1, 110504, 2021.

[17] J. Jayanudin, R. S. D. Lestari, and I. Kustiningsih *et al.*, "Preparation of chitosan microspheres as carrier material to controlled release of urea fertilizer," *South African J. Chem. Eng.*, vol. 38, no. 8, pp. 70–77, 2021.

[18] L. Wang, Y. Chi, K. Du, Z. Zhou, F. Wang, and Q. Huang, "Hydrothermal treatment of food waste for bio-fertilizer production: Formation and regulation of humus substances in hydrochar," *Sci. Total Environ.*, vol. 838, no. 3, 155900, 2022.

[19] S. Wang, Y. Wu, and J. An *et al.*, "geobacter autogenically secretes fulvic acid to facilitate the dissimilated iron reduction and vivianite recovery," *Environ. Sci. Technol.*, vol. 54, no. 17, pp. 10850–10858, 2020.

[20] F. Yang, and M. Antonietti, "The sleeping giant: A polymer view on humic matter in synthesis and applications," *Prog. Polym. Sci.*, vol. 100, 101182, 2020.

[21] M. A. Islam, D. W. Morton, B. B. Johnson, and M. J. Angove, "Adsorption of humic and fulvic acids onto a range of adsorbents in aqueous systems, and their effect on the adsorption of other species: A review," *Sep. Purif. Technol.*, vol. 247, no. 1, 116949, 2020.

[22] J. Li, X. Hao, M. C. M. V. Loosdrecht, Y. Luo, and D. Cao, "Effect of humic acids on batch anaerobic digestion of excess sludge," *Water Res.*, vol. 155, pp. 431–443, 2019.

[23] F. Yang, S. Zhang, K. Cheng, and M. Antonietti, "A hydrothermal process to turn waste biomass into artificial fulvic and humic acids for soil remediation," *Sci. Total Environ.*, vol. 686, pp. 1140–1151, 2019.

[24] L. I. Inisheva, S. G. Maslov, and K. E. Shchukina, "Biochemical activity of peat in the Ob region," *Solid Fuel Chem.*, vol. 52, no. 6, pp. 373–381, 2018.

[25] J. O'Connor, S. A. Hoang, and L. Bradney *et al.*, "A review on the valorisation of food waste as a nutrient source and soil amendment," *Environ. Pollut.*, vol. 272, 115985, 2021.

[26] X. Zhuang, H. Zhan, and Y. Song *et al.*, "Insights into the evolution of chemical structures in lignocellulose and non-lignocellulose biowastes during hydrothermal carbonization (HTC)," *Fuel*, vol. 236, no. 7, pp. 960–974, 2019.

[27] S. A. A. Mohamed, M. El-Sakhawy, and M. A. M. El-Sakhawy, "Polysaccharides, protein and lipid-based natural edible films in food packaging: A review," *Carbohydr. Polym.*, vol. 238, no. 2, 116178, 2020.

[28] M. Tabari, "Investigation of carboxymethyl cellulose (Cmc) on mechanical properties of cold water fish gelatin biodegradable edible films," *Foods*, vol. 6, no. 6, pp. 1–7, 2017.

[29] X. Hu, Y. Liu, D. Zhu, Y. Jin, H. Jin, and L. Sheng, "Preparation and characterization of edible carboxymethyl cellulose films containing natural antibacterial agents: Lysozyme," *Food Chem.*, vol. 385, no. 3, 132708, 2022.

[30] M. Michelin, A. M. Marques, L. M. Pastrana, J. A. Teixeira, and M. A. Cerqueira, "Carboxymethyl cellulose-based films: Effect of organosolv lignin incorporation on physicochemical and antioxidant properties," *J. Food Eng.*, vol. 285, no. 1, 2020.

[31] M. Shahbazi, S. J. Ahmadi, A. Seif, and G. Rajabzadeh, "Carboxymethyl cellulose film modification through surface photo-crosslinking and chemical crosslinking for food packaging applications," *Food Hydrocolloids*, vol. 61, pp. 378–389, 2016.

[32] M. Yildirim-Yalcin, F. Tornuk, and O. S. Toker, "Recent advances in the improvement of carboxymethyl cellulose-based edible films," *Trends in Food Science and Technology*, vol. 129, no. 8, pp. 179–193, 2022.

[33] C. R. Bauli, G. F. Lima, A. G. D. Souza, R. R. Ferreira, and D. S. Rosa, "Eco-friendly carboxymethyl cellulose hydrogels filled with nanocellulose or nanoclays for agriculture applications as soil conditioning and nutrient carrier and their impact on cucumber growing," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 623, no. 3, 126771, 2021.

[34] V. S. Ghorpade, R. J. Dias, K. K. Mali, and S. I. Mulla, "Citric acid crosslinked carboxymethylcellulose-polyvinyl alcohol hydrogel films for extended release of water soluble basic drugs," *Journal of Drug Delivery Science and Technology*, vol. 52, no. 3, pp. 421–430, 2019.

[35] D. Zhang, W. Xu, J. Cai, S. Y. Cheng, and W. P. Ding, "Citric acid-incorporated cellulose nanofibrous mats as food materials-based biosorbent for removal of hexavalent chromium from aqueous solutions," *International Journal of Biological Macromolecules*, vol. 149, pp. 459–466, 2020.

[36] N. Habibi, "Spectrochimica acta part A : Molecular and Biomolecular Spectroscopy Preparation of biocompatible magnetite-carboxymethyl cellulose nanocomposite : Characterization of nanocomposite by FTIR , XRD , FESEM and TEM," *Spectrochim. ACTA PART A Mol. Biomol. Spectrosc.*, vol. 131, pp. 55–58, 2014.

[37] Z. Jiao, B. Zhang, C. Li, W. Kuang, J. Zhang, and Y. Xiong, "Carboxymethyl cellulose-grafted graphene oxide for efficient antitumor drug delivery," *Nanotechnology Reviews*, vol. 7, no. 4, pp. 291–301, 2018.

[38] A. J. Braihi, S. I. Salih, F. A. Hashem, and J. K. Ahmed, "Proposed cross-linking model for carboxymethyl cellulose / starch superabsorbent polymer blend," *International Journal of Materials Science and Applications*, vol. 3, no. 6, pp. 363–369, 2014.

[39] S. Parvaneh, M. Pourmadadi, M. Abdouss, S. Ali, F. Yazdian, A. Rahdar, and A. M. Díez-pascual, "Carboxymethyl cellulose / starch / reduced graphene oxide composite as a pH-sensitive nanocarrier for curcumin drug delivery," *Int. J. Biol. Macromol.*, vol. 241, no. 11, 124566, 2023.

[40] M. Salimi, B. Channab, A. El, and M. Zahouily, "A comprehensive review on starch : Structure , modification , and applications in slow / controlled-release fertilizers in agriculture," *Carbohydr. Polym.*, vol. 322, no. 8, 121326, 2023.